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Reactions of Some Aromatic Hydroxy Compounds with α, ω-Dihaloalkanes in Dimethyl Sulfoxide-Water Mixture

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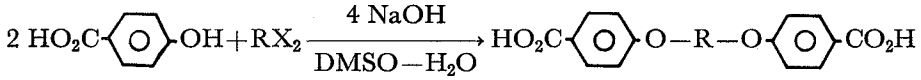
Some α, ω-diphenoxyalkane-*p*, *p*′-dicarboxylic acids (**1**) were prepared by the reaction of *p*-hydroxybenzoic acid with α, ω-dihaloalkane in the presence of NaOH in dimethyl sulfoxide containing considerable amounts of water. This method is adaptable to the preparations of α, ω-diphenoxyalkane-*m*, *m*′-dicarboxylic acids (**2**) and α, ω-diphenoxyalkane-*p*, *p*′-diacetic acids (**3**). Some aromatic polyethers (**4**) could be prepared by the reaction of 4, 4′-isopropylidenediphenol with α, ω-dihaloalkane in the presence of NaOH, in which the dimethyl sulfoxide-water mixture was used in the same manner as a solvent.

Aromatic polyesters[1,2] and polyanhydrides[3] showing excellent film- and fiber-forming properties can be prepared from some of α, ω-diphenoxyalkane-*p*, *p*′-dicarboxylic acids (**1**). Up to date, **1** have mainly been prepared by condensing *p*-hydroxybenzoic acid with the appropriate α, ω-dihaloalkane in an aqueous alkaline solution.[4] For example, α, β-diphenoxyethane-*p*, *p*′-dicarboxylic acid (**1b**) is made by heating *p*-hydroxybenzoic acid with 0.5 molar equivalent of 1, 2-dichloroethane in the presence of 2 molar equivalents of NaOH in water. These acids were also prepared by the reaction of the sodium salt of ethyl *p*-hydroxybenzoate with an alkyl dihalide followed by saponification of the resulting ester.[5]

However, most examples in the above-mentioned literatures give low yields (15–67%) in the condensation step.

Catalytic oxidation of *p*, *p*′-dimethyl-α, ω-diphenoxyalkanes by oxygen gas[6] (or compressed air[7]) in an autoclave seems to be very dangerous.

In the following we report on an improved method for the synthesis of these acids, in which *p*-hydroxybenzoic acid is condensed with the appropriate α, ω-dihaloalkane in the presence of NaOH in dimethyl sulfoxide (DMSO) containing approximately 40% of water. This kind of solvent has already been used as the solvent in the reaction of sodium phenolate with 1, 2-dibromoethane.[8] As Table I indicates, in the cases of the reaction with 1, 2-dibromoethane and with 1, 3-dibromopropane yields are 91% and 97%, respectively, but is poor with dibromomethane.



(**1**)

(**a**) R=$-CH_2-$, X=Br (**b**) R=$-(CH_2)_2-$, X=Br
(**c**) R=$-(CH_2)_3-$, X=Br (**d**) R=$(-CH_2CH_2)_2O$, X=Cl

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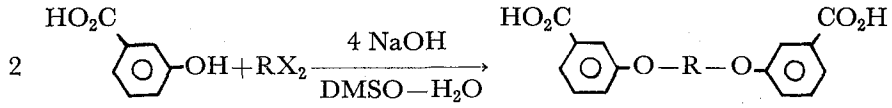
Table I. Syntheses of Some α, ω–Diphenoxyalkane–*p*, *p*′–dicarboxylic Acids (**1**)

R	Reaction conditions		Product[a]		
	Temp. (°C)	Time (hr)	Abbreviation	Yield (%)	Mp[b] (°C) (lit.)
$-CH_2-$	25	10	**1a**	30	288–289 (287–288)[5]
$-(CH_2)_2-$	90	5	**1b**	91	334 (336–338)[14]
$-(CH_2)_3-$	90	9	**1c**	97	309–312 (310–312)[14]
$(-CH_2CH_2)_2O$	90	10	**1d**[c]	68	309–313

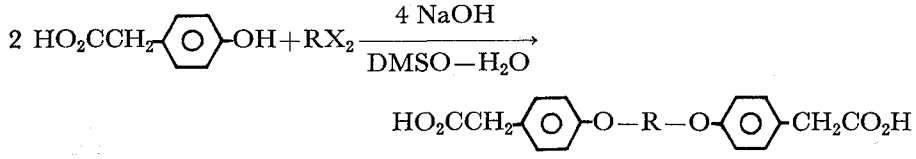
a) All spectral data (NMR, IR) are consistent with the assigned structure of the isolated product. b) It was advantageous to recrystallize the products from hot nitrobenzene. c) *Anal.* Found: C, 62.26; H, 5.41%. Calcd for $C_{18}H_{18}O_7$: C, 62.42; H, 5.24%.

This procedure has been extended to the reaction with *m*–hydroxybenzoic acid and with *p*–hydroxyphenylacetic acid in place of *p*–hydroxybenzoic acid. The results are summarized in Tables II and III.



(**2**)

(a) R=$-CH_2-$, X=Br (b) R=$-(CH_2)_2-$, X=Br
(c) R=$(-CH_2CH_2)_2O$, X=Cl



(**3**)

(**a**) R=$-CH_2-$, X=Br (**b**) R=$-(CH_2)_2-$, X=Br
(**c**) R=$(-CH_2CH_2)_2O$, X=Cl

Table II. Syntheses of Some α, ω–Diphenoxyalkane–*m*, *m*′–dicarboxylic Acids (**2**)

R	Reaction conditions		Product[a]		
	Temp. (°C)	Time (hr)	Abbreviation	Yield (%)	Mp[b] (°C)
$-CH_2-$	25	15	**2a**[c]	47	264–267
$-(CH_2)_2-$	25	15	**2b**[d]	48	291–293
$(-CH_2CH_2)_2O$	70	10	**2c**[e]	58	226–228

a) All spectral data (NMR, IR) are consistent with the assigned structure of the isolated product. b) It was advantageous to recrystallize the products from hot nitrobenzene. c) *Anal.* Found: C, 62.16; H, 4.34%. Calcd for $C_{15}H_{12}O_6$: C, 62.50; H, 4.20%. d) *Anal.* Found: C, 63.70; H, 4.73%. Calcd for $C_{16}H_{14}O_6$: C, 63.57; H, 4.67%. e) *Anal.* Found: C, 62.13; H, 5.23%. Calcd for $C_{18}H_{18}O_7$: C, 62.42; H, 5.24%.

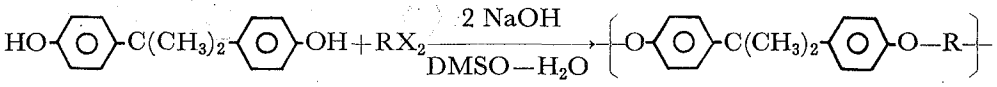
Table III. Syntheses of Some α, ω-Diphenoxyalkane-p, p'-diacetic Acids (**3**)

R	Reaction conditions		Product[a]		
	Temp. (°C)	Time (hr)	Abbreviation	Yield (%)	Mp[b] (°C) (lit.)
$-CH_2-$	50	8	**3a**[c]	46	226–228
$-(CH_2)_2-$	80	3	**3b**	28	256–258 (249–250)[15]
$(-CH_2CH_2)_2O$	70	5	**3c**[d]	82	186–188

a) All spectral data (NMR, IR) are consistent with the assigned structure of the isolated product. b) It was advantageous to recrystallize the products from hot nitrobenzene. c) *Anal.* Found: C, 64.54; H, 5.00%. Calcd for $C_{17}H_{16}O_6$: C, 64.55; H, 5.10%. d) *Anal.* Found: C, 64.35; H, 5.85%. Calcd for $C_{20}H_{22}O_7$: C, 64.16; H, 5.92%.

Among the acids obtained by this procedure, **1b** is most frequently used in the preparation of polyesters by the condensation with aliphatic diols such as ethylene glycol.[9] There are many catalysts effectiving the condensation, namely, TiO_2,[9] $BF_3 \cdot Et_2O$,[10] $TiCl_4$,[10] $FeCl_2$,[10] $SnCl_4$,[10] $AlBr_3$[10], and B_2O_3.[11] The condensation of **1b** with ethylene glycol can also be effected by heating without a catalyst under vacuum at elevated temperatures. We have chosen α, γ-diphenoxypropane-p, p'-dicarboxylic acid (**1c**) among the acids and condensed it with 1, 3-propanediol in the presence of a p-toluenesulfonic acid catalyst. The details are given in experimental section.

In the next place, we report on the reaction of 4, 4'-isopropylidenediphenol with the appropriate α, ω-dihaloalkane in the presence of NaOH in the DMSO–water solvent. To our knowledge, only two cases[12,13] are reported to date on the condensation of 4, 4'-isopropylidenediphenol with an alkyl dihalide in an aqueous solution of NaOH. As Table IV indicates, aromatic polyethers (**4**) of the following formula could be prepared by this low-temperature solution polymerization.



(**4**)

(**a**) R=$-CH_2-$, X=Br (**b**) R=$-(CH_2)_2-$, X=Br
(**c**) R=$-(CH_2)_3-$, X=Br (**d**) R=$(-CH_2CH_2)_2O$, X=Cl

Table IV. Syntheses of Some Polyethers (**4**)

R	Polymerization conditions		Polymer			
	Temp. (°C)	Time (hr)	Abbreviation	Yield (%)	Mp[a] (°C)	η_{inh}[b] (dl/g)
$-CH_2-$	25	5	**4a**	73	90–110	0.22
$-(CH_2)_2-$	25	5	**4b**	96	91–105	0.15
$-(CH_2)_3-$	25	2	**4c**	96	90–115	0.16
$(-CH_2CH_2)_2O$	25	5	**4d**	78	<108	0.13

a) All polymers were reprecipitated from DMSO (or *N*, *N*-dimethylformamide) into methanol (or ethanol). b) Measured at a concentration of 0.2 g/dl in DMSO at 30°C.

EXPERIMENTAL

Illustrative examples of the reactions will be given below.

Condensation of *p*-Hydroxybenzoic Acid with Dibromomethane. To an aqueous alkaline solution prepared from 8.0 g (0.2 mol) of NaOH and 150 ml of water in a 500 ml three neck flask, fitted with a condenser and mechanical stirrer, were added 13.8 g (0.1 mol) of *p*-hydroxybenzoic acid followed by 8.7 g (0.05 mol) of dibromomethane. To dissolve the dibromomethane which went to the bottom of the flask, 200 ml of DMSO was added with stirring. The homogeneous mixture thus obtained was stirred at room temperature (25°C) for 10 hr. The mixture was then poured into a large quantity of water and filtered. The filtrate was acidified to congo red with 10% HCl to precipitate the product. When the precipitate was filtered, washed with a small amount of water, and dried at 100°C, a product of high purity was obtained. One recrystallization from nitrobenzene gave an analytically pure product.

Condensation of α, γ-Diphenoxypropane-p,p'-dicarboxylic Acid (1c) with 1, 3-Propanediol. A mixture of 1.7 g (5.4 mmol) of **1c**, 5.0 g (66 mmol) of 1, 3-propanediol and 0.1 g of *p*-toluenesulfonic acid was placed in a side arm test tube equipped with a gas inlet tube through which nitrogen was led in. The mixture was heated at 150°C for 3 hr and further at 200°C for 10 hr, during which time stirring was applied. After cooling the mixture was washed thoroughly with water and the residue was placed again in another side arm test tube of similar type. A nitrogen atmosphere was maintained throughout, and the mixture was heated at 200°C/5 mmHg for 8 hr and further at 250°C/1 mmHg for 3 hr. The viscous mass which resulted was cooled and dissolved in *N*, *N*-dimethylformamide, filtered, precipitated into methanol and collected by filtration. Yield: 1.5 g (78%), mp<100°C. The inherent viscosity was 0.16 in dioxane (0.2 g/dl at 30°C).

Condensation of 4, 4'-Isopropylidenediphenol with Dibromomethane. To 30 ml of water in a 200 ml round bottom flask, fitted with a condenser and mechanical stirrer, were added 1.6 g (40 mmol) of NaOH followed by 4.6 g (20 mmol) of 4, 4'-isopropylidenediphenol and 3.5 g (20 mmol) of dibromomethane. The mixture was stirred at room temperature (25°C) for some time. Following this, 50 ml of DMSO was added to the mixture in order to dissolve the dibromomethane which remained in the bottom of the flask. The homogeneous mixture thus obtained was stirred at room temperature for 5 hr. The solvent was distilled *in vacuo*, and the residue was taken up in DMSO, filtered, and precipitated into methanol.

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